other silica system particles -- sol etc. is used. Furthermore, the particles which consist of porosity zeolite which removed the aluminium from the zeolite which consists of aluminosilicate can also be used. As for the silica system particles used by this invention, it is desirable for the mean particle diameter to be 5-50nm within the limits of 10-50nm preferably. As long as it is the particles of the grain size which is within the limits of this, the things of a uniform grain size may also be two or more kinds of mixtures of particles with which grain sizes differ. Moreover, it may be a globular form or you may be a variant. In less than 5nm, this grain size will tend to produce a defect at the time of micro processing in the micro photo lithography process of the coat obtained from the coating liquid manufactured from this, if the stability of the coating liquid manufactured from this with the passage of time becomes scarce and exceeds 50nm on the other hand.

[0031] The polysiloxane used by this invention mixes one or more sorts of silicon compounds chosen from the group which consists of halogenation Silang expressed with the alkoxysilane expressed with such silica system particles and the above-mentioned general formula (I), and the above-mentioned general formula (II) in an organic solvent. It is made to hydrolyze under existence of water and a catalyst. It is obtained. As halogenation Silang expressed with the alkoxysilane expressed with a general formula (I), and a general formula (II), what was illustrated in the aforementioned (A) silicon compound and its hydrolyzate, and the same thing are mentioned.

[0032] Such a preparation method of polysiloxane can be prepared according to the method indicated in gazettes, such as said invention-1 (refer to JP,H9-315812,A) for which these people applied, or said invention-3 (international application PCT/JP99/04050 reference). One or more sorts of halogenation Silang specifically shown with the alkoxysilane and the general formula (II) which are shown with the above-mentioned silica system particles and a general formula (I) are mixed in an organic solvent, and it is obtained by performing the hydrolysis reaction of alkoxysilane and halogenation Silang under existence of water and a catalyst.

[0033] As alkoxysilane shown with said general formula (I), what was illustrated by said silica system particle, and the same thing are mentioned. The alkoxysilane used for a hydrolysis may be the same as what was used at the time of silica system particle preparation, or may differ. As an organic solvent, aromatic hydrocarbon other than what was illustrated by preparation of said silica system particle, and the same thing, such as hydrocarbons, such as hexane, cyclohexane, and octane, toluene, xylene, and mesitylene, is mentioned.

[0034] As a catalyst, the compound in which acidity is shown in aqueous solutions, such as organic acids, such as inorganic acids, such as hydrochloric acid, nitric acid, and sulfuric acid, acetic acid, oxalic acid, and toluenesulfonic acid, or metal soap, is mentioned. Water required for the hydrolysis reaction of an ARUKO gardenia fruit run or halogenation Silang, Si-X machine 1 mol which constitutes the Si-OR machine 1 mol or halogenation Silang which

constitutes alkoxysilane (when mixing and using alkoxysilane and halogenation Silang) The thing of a Si-OR machine and a Si-X machine for which the sum total hits and 0.1-5mol is usually preferably used in the quantity of 0.1-2mol is desirable. Moreover, as for a catalyst, it is desirable to be added in the quantity of 0.001-1mol per alkoxysilane or 1mol of halogenation Silang (it is the total quantity when mixing and using alkoxysilane and halogenation Silang).
[0035] When both the mixed rates (S/T) of the silica system particles (alkoxysilane shown with S) and said general formula (I) and/or halogenation Silang (T) used for preparation of polysiloxane are converted SiO2 It is desirable 1 / 99 - 10/90, and that it is in the range of 1 / 99 - 5/95 preferably at ********. The stability of the polysiloxane from which a hydrolysis reaction advances and this mixed rate (S/T) is obtained by less than 1/99 besides the surface of silica system particles with the passage of time may become scarce. Moreover, when there are more these mixed rates (S/T) than 10/90, the bonding strength of the polysiloxane obtained becomes weak and there is a tendency it becomes impossible to maintain sufficient film hardness.
[0036] Although the reaction conditions in particular in this process are not restricted, about 100 degrees C or less, it is usually desirable [it is 80 degrees C or less in temperature preferably, and / agitating] to carry out over 0.5 to 3 hours preferably for 0.5 to 5 hours. Thereby, the polysiloxane to which the hydrolyzate of alkoxysilane or halogenation Silang reacted to the surface of silica system particles is obtained.
[0037] However, about the preparation methods of this polysiloxane, it is not limited above and the polysiloxane manufactured by the method given in JP,H9-315812,A etc. can also be used.
(D) The coating liquid for low permittivity silica system coat formation concerning easily decomposability resin this invention may contain easily decomposability resin further.
[0038] It decomposes or vaporizes by having the number average molecular weight (polystyrene conversion) of 500-50,000 as easily decomposability resin, irradiating heat treatment or ultraviolet radiation, an infrared radiation, electron rays, and X-rays at the temperature of 500 degrees C or less, or irradiating oxygen plasma. As the example of such easily decomposability resin ** and a number average molecular weight (polystyrene conversion) -- 500-50,000 -- desirable -- cellulose system resin of 5,000-30,000 -- Polyamide system resin, polyester system resin, acrylic resin, polyether system resin, polyolefine system resin, polyol system resin, epoxy system resin, etc. are mentioned.
[0039] Moreover, in the coating liquid for low permittivity silica system coat formation of this invention, it is desirable that the easily decomposability resin (aforementioned [D]) constitutes the mutual intrusion type polymer composition which became entangled with the aforementioned (A) silicon compound (hydrolyzate) or the aforementioned (C) polysiloxane on the chain level. As for the number average molecular weight (polystyrene conversion) of such a mutual intrusion type polymer composition, it is desirable 500-50,000 and that it is in the

range of 1,000-30,000 preferably.
[0040] About the preparation methods of such a mutual intrusion type polymer composition, the details are indicated in the gazette of invention-2 (international application PCT/JP99/04051) for which these people applied, or said invention-3 (international application PCT/JP99/04050). Such a polymer composition can be prepared by mixing the aforementioned (A) silicon compound (hydrolyzate) and/or (C) polysiloxane, and (D) easily decomposability resin in organic solvents, such as ketone, ether, ester, hydrocarbons, and aromatic hydrocarbon. In this case, in this organic solvent, one sort of the alkoxysilane shown with said general formula (I) if needed or two sorts or more can be added.
[0041] (A) As for the solution (dispersion liquid) which mixed a silicon compound (hydrolyzate), and/or (C) polysiloxane and (D) easily decomposability resin, it is desirable under existence of a little water and an acid catalyst to agitate at the temperature of 20-60 degrees C for 1 to 6 hours. the (A) silicon compound (hydrolyzate) and/or the secondary hydrolysis reaction of polysiloxane advance in an easily decomposability resin frame by this -- the (A) silicon compound (hydrolyzate) and/or (C) polysiloxane, (D) The polymer composition with which easily decomposability resin became entangled uniformly is obtained. However, in this method, the polymer composition which became entangled uniformly according to the kind of easily decomposability resin etc. may not be obtained.
[0042] Moreover, a polymer composition can be prepared alkoxysilane or halogenation Silang, easily decomposability resin, and if needed by carrying out the contact hydrolysis reaction of the silica system particles using an incompatible organic solvent and water. According to this preparation method method, a mutual intrusion type polymer composition can be formed easily directly. The coating liquid of this invention is the aforementioned (A) silicon compound (it is the same after containing also in hydrolyzate) shown above, It is desirable to contain preferably solid content, such as the organic template material (aforementioned [B]) and the arbitrary and included aforementioned (C) polysiloxane, a constituent containing the easily decomposability resin (aforementioned [D]), and the above mentioned mutual intrusion type polymer composition, in 10 to 30weight % of quantity five to 35weight % in an organic solvent.
[0043] It can be used as said organic solvent, choosing from organic solvents, such as alcohols, glycol ethers, ketone, ether, ester, hydrocarbons, and aromatic hydrocarbon. Below, the semiconductor board with a low permittivity silica system coat of this invention is explained concretely.
[0044] [Semiconductor board with a low permittivity silica system coat] Semiconductor board with a low permittivity silica system coat concerning this invention, The silicon substrate by which it comes to prepare a low permittivity silica system coat in a part for the element surface and/or PN junction between the wiring layers of multilevel interconnection structure on a silicon substrate, It is the semiconductor board with a low permittivity silica system coat which

consists of a multilayer wiring layer on a silicon substrate, and a low permittivity silica system coat, and after a low permittivity silica system coat applies said coating liquid for low permittivity silica system coat formation and subsequently heat-treats it, it is characterized by being obtained by carrying out baking treatment.

[0045] The silica system coat formed on this silicon substrate, A dielectric constant is as small as 2.5 or less, and, moreover, it excels in chemical resistance, such as adhesion with a coated side, and alkali resistance, or crack-proof nature, and it not only also has process conformity, such as acid-proof matter plasma nature and etching processing nature, further, but has remarkable low water adsorption nature and coat hardness high enough.

[0046] This low permittivity silica system coat applied the above mentioned coating liquid for low permittivity silica system coat formation, and was formed. It is and consists of a silica system component which uses as a precursor hydrolyzate of one or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are shown with a following general formula (I).

XnSi(OR)4-n (I) XnSiX'4-n (II) (the inside of a formula, and X -- a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group) It expresses, R expresses a hydrogen atom or the alkyl group of a carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom. Moreover, n is the integer of 0-3.

As an example of halogenation Silang shown with the alkoxysilane shown with said general formula (I), and said general formula (II), the same thing is mentioned with having described above.

[0047] Polysiloxane which is the reactant of the hydrolyzate of one or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane shown with said general formula (I) and said general formula (II), and silica system particles may be included in such a silica system coat. It is desirable that such polysiloxane is included in 5 to 90weight % of the range by oxide (SiO2) conversion in a coat. It is 20 to 80weight % of a range still more preferably. If polysiloxane is included in said range, the dielectric constant of a coat can obtain the silica system coat excellent in a heat-resisting property, hardness, etc. or less by 2.5.

[0048] In addition, with heating at the time of coat formation, it vaporized or decomposed and the organic template material and easily decomposability resin which were added by coating liquid have disappeared. Next, it illustrates concretely about the formation method of the low permittivity silica system coat on a semiconductor board. Restriction in particular does not have formation of a low permittivity silica system coat, and it can adopt a well-known method conventionally. for example, (a) -- [the coating liquid / the above coating liquid for low

permittivity silica system coat formation is applied on a semiconductor board and] (b) After heat-treating the obtained coat at the temperature of 350 degrees C or less, it can form by carrying out baking treatment of the (c) this coat at the temperature of 350-450 degrees C under the atmosphere of inert gas.

[0049] (a) Although coater is generally adopted for the spin coat method, the dip coating method, the roll coat method, the decalcomania method, etc. as the spreading method of such coating liquid, Also in this invention method, the coating liquid for low permittivity silica system coat formation can be applied on a semiconductor board using such a conventionally well-known method.

[0050] (b) 350 degrees C or less of coats applied on heat-treatment, thus a semiconductor board are preferably heat-treated at the temperature of 50-300 degrees C. Although this heating changes with thickness of a coat etc., it is desirable to carry out over 2 to 5 minutes preferably for 1 to 10 minutes. Although this heat-treatment may be performed under inert gas atmosphere, such as nitrogen, like before, it is desirable to carry out under air atmosphere. This is because this treatment is performed short time under temperature conditions comparatively as low as 350 degrees C or less, so the damage by metal oxidation etc. will not be given to the metal wiring arranged on the semiconductor board even if it heat-treats oxygen under the air atmosphere included comparatively so much. Since a possibility that can reduce the amount of the expensive nitrogen gas used by this, and a small amount of oxygen will be incorporated into a coat increases, SiO2 to which bridge formation of Si-O-Si binding progressed on the occasion of latter (c) baking treatment It generates and becomes easy to form the low permittivity silica system coat which has low-water-flow part adsorbent and high coat hardness.

[0051] While the organic solvent contained in a coat by heat-treating as mentioned above evaporates Organic template material ****s, and on the other hand, while the polymerization of a formed element progresses and hardens, the melt viscosity of a polymer falls in process of heating, the reflow nature of a coat increases, and the evenness of the coat obtained improves. Thus, although the thickness of the low permittivity silica system coat formed changes also with the semiconductor board which forms a coat, or its purposes, it is usually about 100-600nm on the silicon substrate in a semiconductor device, for example. In between the wiring layers of multilevel interconnection, it is usually 100-1,000nm.

[0052] (c) calcination **** -- as for the coat given said heat-treatment, subsequently, it is desirable under the atmosphere of inert gas to carry out baking treatment (cure) at the temperature of 350-450 degrees C. As said inert gas, desirably, using nitrogen gas may add oxygen gas or air to this, and it may use as inert gas containing a small amount of oxygen if needed further.

[0053] Although the aforementioned burning temperature changes with descriptions of Si

content compound (silica system component) contained in the kind of organic template material used for coating liquid, quantity, or coating liquid etc., it is chosen from a 350-450-degree C range. if it is this range -- low-water-flow part adsorbent -- the film-ed [low permittivity silica system] of high coat hardness -- it can obtain. Furthermore, if it is required to carry out at the above temperature to which this easily decomposability resin decomposes or vaporizes and it is a 350-450-degree C range also when the coating liquid containing easily decomposability resin is used, they are organic template material and/or easily decomposability resin. The low permittivity silica system coat of high intensity is formed by the low density in which a matrix has only the hole of a diameter of 5nm or less substantially.
[0054] Moreover, although this baking treatment changes with the kind of coating liquid, thickness of a coat, etc., it is desirable to carry out over 10 to 60 minutes. Since bridge formation of the precursor of a silica system component cannot advance easily that the temperature of baking treatment is less than 350 degrees C here, if the coat which has sufficient coat hardness is not obtained and the temperature of baking treatment exceeds 450 degrees C, Since aluminium wiring, copper wiring, etc. which constitute a semiconductor board oxidize, or it is fused and damage may be done to this wiring layer, as for the temperature concerned, it is desirable to maintain at the range of 350-450 degrees C.
[0055]
[Effect of the Invention] The coating liquid for low permittivity silica system coat formation of this invention serves as a precursor of a specific silica system component, and organic template material from easily decomposability resin if needed. Bridge formation of a silica system component precursor runs, and although the coat obtained is a low density in porosity, it can obtain the low permittivity silica system coat of high coat hardness.
[0056] The semiconductor board with a low permittivity silica system coat of this invention, [a part for the element surface and/or PN junction] between the wiring layers of multilevel interconnection structure on a silicon substrate [the coat which are the parts for semiconductor devices with which the low permittivity silica system coat was formed, and was formed on this semiconductor board] Since it is formed using the coating liquid for low permittivity silica system coat formation of this invention, adhesion with a coated side, It excels in chemical resistance, such as alkali resistance, or crack-proof nature, and it not only also has process conformity, such as acid-proof matter plasma nature and etching processing nature, further, but has remarkable low water adsorption nature and coat hardness high enough.
[0057]
[Example] Hereafter, although an example explains this invention, this invention is not limited to these examples.
[0058]
[Example 1] An Ethanol [of the coating liquid for coat formation (S-1) / the preparation

triethoxysilane (made by Shin-Etsu Chemical) 80.0g, methyl trimetoxysilane (made by Shin-Etsu Chemical) 68.18g, and Ethanol 451.82g] mixed solution is held at 20 degrees C. While adding 54.0g of nitric acid content aqueous solutions of concentration to this at once 0.05weight % and agitating at velocity of 150rpm The hydrolysis of triethoxysilane and methyl trimetoxysilane was performed at the temperature of 20 degrees C for about 1 hour. Then, 1.5-times the amount propyl propylene glycol (PFG) is added, and solvent displacement is carried out at propyl propylene glycol (PFG) using a rotating evaporator, The alcohol generated by the hydrolysis reaction and the moisture (nitric acid is included) which dissolved were removed completely, and silica concentration obtained the hydrolyzate (matrix precursor PFG dispersion liquid) of the triethoxysilane which is 20 weight %, and methyl trimetoxysilane.

[0059] To 100g of the PFG solution of the matrix precursor obtained as mentioned above, it is organic template material. 25g of methanol solution of n-hexadecyl trimethylammonium high draw KISAIDO (n-HDTMAH) of 20 weight % of concentration was mixed, and 125g of coating liquid for coat formation (S-1) was obtained.

The coating liquid for coat formation (S-1) which is the manufacture above of a semiconductor board with a silica system coat (L-1), and was made and prepared was applied to the 8-inch silicon wafer (semiconductor board) with the spin coat method, respectively.

[0060] Then, the heat-treatment process was presented with the substrate and it was heated for 3 minutes at the temperature of 150 degrees C under air atmosphere. In this heat-treatment, since the organic solvent contained in a coat evaporated, this was exhausted out of the system. Subsequently, under nitrogen-gas-atmosphere mind, for 30 minutes and baking treatment were performed at the temperature shown in Table 1, and the semiconductor board with a silica system coat (L-1) was manufactured. Next, it cooled to the temperature near the room temperature, and took out out of the system.

[0061] Thus, the thickness of the obtained coat was 5,000A. Subsequently, the dielectric constant of the obtained silica system coat (the mercury probe method, frequency of 1MHz), The amount change of water adsorption of the coat before and behind an oxygen plasma exposure (the TDS method: Thermal Desorption Mass-Spectroscopy), The existence (change of a wiring resistance value is measured with a tester) of damage to the metal wiring on coat hardness (Sebastian strength test machine) and a substrate was measured.

[0062] A result is shown in Table 1.

[0063]

[Example 2] To 100g of PFG dispersion liquid of the matrix precursor prepared like the preparation examples 1 of the coating liquid for coat formation (S-2), it is organic template material. 75g of methanol solution of n-hexadecyl trimethylammonium high draw KISAIDO of 20 weight % of concentration was mixed, and 175g of coating liquid for coat formation (S-2) was obtained.

[0064] The semiconductor board with a silica system coat (L-2) was manufactured like the example 1 except having used each coating liquid for coat formation (S-2) which is the manufacture above of a semiconductor board with a silica system coat (L-2), and was made and prepared. The thickness of the obtained coat was 5,000A. Subsequently, the existence of damage to the metal wiring on the amount change of water adsorption of the dielectric constant of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat hardness, and a substrate was measured.
[0065] A result is shown in Table 1.
[0066]
[Example 3] To 80g of PFG solutions of the matrix precursor prepared like the preparation examples 1 of the coating liquid for coat formation (S-3), it is the acrylate resin of 20 weight % of concentration (number average molecular weight). 20g of PFG solutions of 22,190 were mixed, subsequently to this, 20g of methanol solution of n-hexadecyl trimethylammonium high draw KISAIDO (n-HDTMAH) of 20 weight % of concentration was mixed as organic template material, and 120g of coating liquid for coat formation (S-3) was obtained.
[0067] The semiconductor board with a silica system coat (L-3) was manufactured like the example 1 except having used each coating liquid for coat formation (S-3) which is the manufacture above of a semiconductor board with a silica system coat (L-3), and was made and prepared. The thickness of the obtained coat was 5,000A. Subsequently, the existence of damage to the metal wiring on the amount change of water adsorption of the dielectric constant of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat hardness, and a substrate was measured.
[0068] A result is shown in Table 1.
[0069]
[Example 4] To 66.67g of PFG dispersion liquid of the matrix precursor prepared like the preparation examples 1 of the coating liquid for coat formation (S-4), it is the acrylate resin of 20 weight % of concentration (number average molecular weight). 33.33g of PFG solutions of 22,190 are mixed. Subsequently, 16.67g of methanol solution of n-hexadecyl trimethylammonium high draw KISAIDO (n-HDTMAH) of 20 weight % of concentration was mixed as organic template material to this, and 116.67g of coating liquid for coat formation (S-4) was obtained.
[0070] The semiconductor board with a silica system coat (L-4) was manufactured like the example 1 except having used the coating liquid for coat formation (S-4) which is the manufacture above of a semiconductor board with a silica system coat (L-4), and was made and prepared. The thickness of the obtained coat was 5,000A. Subsequently, the existence of damage to the metal wiring on the amount change of water adsorption of the dielectric constant of a silica system coat and the coat before and behind an oxygen plasma exposure,

coat hardness, and a substrate was measured.
[0071] A result is shown in Table 1.
[0072]
[Example 5] Except having used n-octadecyl trimethylammonium high draw KISAIDO (n-ODTMAH) as organic template material, the coating liquid for coat formation (S-5) was prepared like the example 4, and, subsequently the semiconductor board with a silica system coat (L-5) was manufactured. The existence of damage to the metal wiring on the amount change of water adsorption of the dielectric constant of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat hardness, and a substrate was measured.
[0073] A result is shown in a table.
[0074]
[Comparative example 1] Except not having used organic template material, the coating liquid for coat formation was prepared like the example 1, and, subsequently the semiconductor board with a silica system coat was manufactured. The existence of damage to the metal wiring on the amount change of water adsorption of the dielectric constant of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat hardness, and a substrate was measured.
[0075] A result is shown in Table 1.
[0076]
[Comparative example 2] Except not having used organic template material, the coating liquid for coat formation was prepared like the example 4, and, subsequently the semiconductor board with a silica system coat was manufactured. The existence of damage to the metal wiring on the amount change of water adsorption of the dielectric constant of the obtained silica system coat and the coat before and behind an oxygen plasma exposure, coat hardness, and a substrate was measured.
[0077] A result is shown in Table 1.
[0078]
[Table 1]

表1

	被膜形成用塗布液								焼成工程加熱温度(℃)	被膜付基板の特性			
	マトリックス前駆体		有機テンプレート			易分解性樹脂溶液							
	分散液重量(g)	濃度重量%	種類	溶液重量(g)	濃度重量%	種類	溶液重量(g)	濃度重量%		比誘電率	水分吸着量	被膜強度(Mpa)	金属配線への損傷の有無
実施例1	100	20	n-HDTMAH	25	20	-	-	-	425	2.5	少	>70	無
実施例2	100	20	n-HDTMAH	75	20	-	-	-	425	2.0	少	50	無
実施例3	80	20	n-HDTMAH	20	20	アクリル樹脂	20	20	425	2.3	少	60	無
実施例4	66.67	20	n-HDTMAH	16.67	20	アクリル樹脂	33.33	20	425	2.1	少	55	無
実施例5	66.67	20	n-ODTMAH	16.67	20	アクリル樹脂	33.33	20	425	2.0	少	50	無
比較例1	100	20	使用せず			-	-	-	425	3.5	少	>70	無
比較例2	66.67	20	使用せず			アクリル樹脂	33.33	20	500	3.3	多	>70	有

[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2002-030249**

(43)Date of publication of application : **31.01.2002**

(51)Int.Cl. C09D183/04
C09D183/08
H01L 21/312

(21)Application number : **2000-214438**

(22)Date of filing : **14.07.2000**

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(54) SILICA COATING LIQUID FOR FORMING LOW DIELECTRIC CONSTANT AND SILICA COAT SUBSTRATE WITH LOW DIELECTRIC CONSTANT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a silica coating liquid for forming low-dielectric constant with a dielectric constant as small as ≤2.5, having low moisture absorbability and high mechanical strength.

SOLUTION: This coating liquid contains (A) at least one silicon compound selected from the group consisting of alkoxysilanes of the general formula (I): XnSi(OR)4-n and silane halides of the general formula (II): XnSiX'4-n and (B) an organic template material of the general formula (III): [R1R2R3R4N]+Y- (in these formulas, X is H, F, a 1-8C alkyl, fluorine-substituted alkyl, aryl or vinyl; R is H, a 1-8C alkyl, aryl or vinyl; X' is a halogen atom; n is an integer of 0-3; R1 is a 1-20C hydrocarbon group; R2 to R4 are each H or a 1-20C hydrocarbon group and may be the same as R1; and Y is a halogen atom or OH).

LEGAL STATUS

[Date of request for examination] 29.07.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or

application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

JP. 2002-030249.

CLAIMS

[Claim(s)]

[Claim 1] Coating liquid for low permittivity silica system coat formation characterized by providing the following (A) One or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are shown with a following general formula (I), and/or its hydrolyzate (B) Organic template material expressed with a following general formula (III)

XnSi(OR)4-n (I)XnSiX'4-n (II)[R1R2R3R4N]+Y- (III)

(X express a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of a carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3. Moreover, carbon numbers may differ mutually, or the hydrocarbon group of 1-20, R2, R3, and R4 may have them, and H atom or a carbon number may be the hydrocarbon group of 1-20, and that of R1 may be still the same as that of R1. [same] Y shows a halogen atom or OH group.

[Claim 2] Coating liquid for low permittivity silica system coat formation according to claim 1 characterized by providing the following The aforementioned (A) silicon compound and/or its hydrolyzate (B) [agent / organic template] (C) Polysiloxane which is the reactant of one or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are shown with a following general formula (I) and/or its hydrolyzate, and silica system particles

XnSi(OR)4-n (I) XnSiX'4-n (II) (among a formula) X expresses a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group, R expresses a hydrogen atom or the alkyl group of a carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom. Moreover, n is the integer of 0-3.

[Claim 3] Furthermore, coating liquid for low permittivity silica system coat formation according to claim 1 or 2 characterized by including (D) easily decomposability resin.
[Claim 4] The easily decomposability resin (aforementioned [D]) is coating liquid for low permittivity silica system coat formation according to claim 3 characterized by constituting the mutual intrusion type polymer composition which became entangled with the aforementioned (A) silicon compound and/or its hydrolyzate, or the aforementioned (C) polysiloxane on the chain level.
[Claim 5] The silicon substrate by which it comes to prepare a low permittivity silica system coat in a part for the element surface and/or PN junction between the wiring layers of multilevel interconnection structure on a silicon substrate The multilayer wiring layer on a silicon substrate Low permittivity silica system coat It is the semiconductor board with a low permittivity silica system coat equipped with the above, and after a low permittivity silica system coat applies the coating liquid for low permittivity silica system coat formation according to claim 1 to 4 and subsequently heat-treats it, it is characterized by being obtained by carrying out baking treatment.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] The dielectric constant of this invention is as small as 2.5 or less, and it relates to the semiconductor board with which the low permittivity silica system coat this coat which has the coating liquid and such characteristics for forming the low permittivity silica system coat which moreover has low-water-flow part adsorbent and the characteristics of high coat hardness was formed.
[0002]
[Background of the Invention] In the semiconductor device below the 0.25-micron Ruhr which has multilevel interconnection with high integration of a semiconductor device, since a metal wiring interval becomes narrow, the impedance of the metal wiring by electrostatic induction increases, and we are anxious about the delay of speed of response, increase of power consumption, etc. For this reason, to make as small as possible the dielectric constant of the interlayer insulation film prepared between a semiconductor board and metallic wiring layers, such as an aluminium wiring layer, or between metallic wiring layers is needed.
[0003] The interlayer insulation film used for the above purpose is formed on the semiconductor board by the method of application which generally forms an insulating film using vapor growth, such as a CVD method, or the coating liquid for coat formation. However, in vapor growth, such as a CVD method, there is a problem that it is difficult to call 3.5 of fluorine dope silica membrane limit, and for the dielectric constant of the silica system coat

obtained to form three or less silica system coat. Moreover, CVD coats, such as poly aryl resin, fluoridation polyimide resin, and fluororesin, and the coat formed using these coating liquid, Although a dielectric constant becomes around two, adhesion with a coated side is bad, and adhesion with the resist material used for micro processing also has it, and there are problems, such as being further inferior to chemical resistance, acid-proof matter plasma nature, etc.
[bad]

[0004] In the coating liquid for silica system coat formation which contains the partial hydrolysis thing or hydrolyzate of alkoxysilane or halogenation Silang used from the former further again, although around 2.5 coats are obtained for a dielectric constant, there is a problem that adhesion with a coated side is bad. In order that this invention persons might solve these problems, a place [it inquired wholeheartedly], If the coating liquid for low permittivity silica system coat formation as shown below is used, a dielectric constant is as small as three or less. And it found out that the coat which was excellent in chemical resistance, such as adhesion with a coated side, mechanical strength, and alkali resistance, or crack-proof nature, and was further excellent also in process conformity, such as acid-proof matter plasma nature and etching processing nature, could be formed, and has applied for these invention.

(1) Invention-1 (refer to JP,H9-315812,A).

[0005] Coating liquid for low permittivity silica system coat formation containing alkoxysilane and/or halogenation Silang or such hydrolyzates, and a reactant with silica particles.

(2) Invention-2 (refer to international application PCT/JP99 / 04051 gazettes)

Coating liquid for low permittivity silica system coat formation containing alkoxysilane and/or halogenation Silang or such hydrolyzates, and the readily decomposable resin that decomposes or vaporizes at the temperature of 500 degrees C or less.

(3) Invention-3 (refer to international application PCT/JP99 / 04050 gazettes)

Coating liquid for low permittivity silica system coat formation containing polysiloxane which is the reactant of alkoxysilane and/or halogenation Silang, or these hydrolyzate and silica particles, and the readily decomposable resin which decomposes or vaporizes at the temperature of 500 degrees C or less.

[0006] Then, this invention persons are these coating liquid and the well-known coat forming method conventionally. The place performed by repeating the examination which uses and forms a low permittivity silica system coat on various semiconductor boards, Although the coat which has the aforementioned characteristics was obtained, forming stably the coat which has the outstanding characteristics that a dielectric constant is 2.5 or less, water adsorption nature is low, and coat hardness is high found out the difficult thing.

[0007] And this invention persons are one or more sorts of silicon compounds chosen from the group which consists of (A) alkoxysilane and halogenation Silang when research is continued further wholeheartedly, and/or its hydrolyzate, (B) When forming the low permittivity silica

system coat on the semiconductor board using the coating liquid for low permittivity silica system coat formation containing an organic template agent, it finds out that the above problems are easily solvable, and came to complete this invention.

[0008]

[Objects of the Invention] This invention tends to solve the above problems. [without giving a damage to the metal wiring which exists and was arranged on the semiconductor board] The coating liquid for low permittivity silica system coat formation and this coating liquid which can form the low permittivity silica system coat which a dielectric constant is as small as 2.5 or less, is moreover low-water-flow part adsorbent, and has the outstanding characteristics of having high coat hardness are applied. It aims at offering the semiconductor board with which the low permittivity silica system coat obtained by carrying out desiccation etc. was formed.

[0009]

[Summary of the Invention] Coating liquid for low permittivity silica system coat formation of this invention, (A) Coating liquid for low permittivity silica system coat formation containing one or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are shown with a following general formula (I) and/or its hydrolyzate, and (B) organic template agent.

[0010] (B) Coating liquid for low permittivity silica system coat formation containing the organic template material expressed with a following general formula (III).

XnSi(OR)4-n (I)XnSiX'4-n (II)[R1R2R3R4N]+Y- (III)

(X express a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group among a formula, R expresses a hydrogen atom or the alkyl group of a carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom.) Moreover, n is the integer of 0-3.

[0011] Moreover, carbon numbers may differ mutually, or the hydrocarbon group of 1-20, R2, R3, and R4 may have them, and H atom or a carbon number may be the hydrocarbon group of 1-20, and that of R1 may be still the same as that of R1. [same] Y shows a halogen atom or OH group.

Said coating liquid for low permittivity silica system coat formation is [the aforementioned (A) silicon compound and/or its hydrolyzate, and] (B) organic template agent, (C) It is characterized by including polysiloxane which is the reactant of one or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are shown with a following general formula (I) and/or its hydrolyzate, and silica system particles.

[0012] XnSi(OR)4-n (I) XnSiX'4-n (II) (the inside of a formula, and X -- a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group) It expresses, R expresses a hydrogen atom or the alkyl group of a

carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom. Moreover, n is the integer of 0-3.

It is desirable that (D) easily decomposability resin is further contained in the coating liquid for low permittivity silica system coat formation concerning this invention.

[0013] As for such (D) easily decomposability resin, it is desirable to constitute the mutual intrusion type polymer composition which became entangled with the (A) silicon compound and/or its hydrolyzate, or (C) polysiloxane on the chain level. The semiconductor board with a low permittivity silica system coat of this invention, The silicon substrate by which it comes to prepare a low permittivity silica system coat in a part for the element surface and/or PN junction between the wiring layers of multilevel interconnection structure on a silicon substrate, It is the semiconductor board with a low permittivity silica system coat which consists of a multilayer wiring layer on a silicon substrate, and a low permittivity silica system coat, and after a low permittivity silica system coat applies said coating liquid for low permittivity silica system coat formation and subsequently heat-treats it, it is characterized by being obtained by carrying out baking treatment.

[0014]

[Detailed Description of the Invention] The coating liquid for low permittivity silica system coat formation of this invention is explained concretely hereafter.

[Coating liquid for low permittivity silica system coat formation] Coating liquid for low permittivity silica system coat formation by this invention, (A) One or more sorts of silicon compounds chosen from the group which consists of alkoxysilane and halogenation Silang and/or its hydrolyzate, and (B) organic template material are distributing or dissolving in water and/or an organic solvent.

[0015] (A) As a silicon compound, and the hydrolyzate silicon compound and its hydrolyzate, One or more sorts of silicon compounds chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are shown with a following general formula (I), and/or its hydrolyzate are used.

XnSi(OR)4-n (I) XnSiX'4-n (II) (the inside of a formula, and X -- a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group) It expresses, R expresses a hydrogen atom or the alkyl group of a carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom. Moreover, n is the integer of 0-3.

As the example of alkoxysilane shown with said general formula (I), Methyl trimetoxysilane, methyltriethoxysilane, methyl triisopropoxy silane, Ethyltrimethoxysilane, ethyltriethoxysilane, ethyl triisopropoxy silane, Octyl trimethoxysilane, octyl triethoxysilane, vinyltrimetoxysilane, Vinyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, Trimethoxysilane, triethoxysilane, triisopropoxy silane, Fluoro trimethoxysilane, fluoro triethoxysilane,

dimethyldimethoxysilane, Dimethyldiethoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, Dimethoxysilane, diethoxysilane, difluoro dimethoxysilane, difluoro diethoxysilane, trifluoromethyl trimethoxysilane, trifluoromethyl triethoxysilane, etc. are mentioned.

[0016] As the example of halogenation Silang shown with said general formula (II), Trichlorosilane, tribromo silane, dichlorosilane, fluoro trichlorosilane, fluoro bromo silane, methyltrichlorosilane, ethyltrichlorosilane, phenyl trichlorosilane, vinyl trichlorosilane, etc. are mentioned. Set above. When using the hydrolyzate of alkoxysilane and/or halogenation Silang [the organic solvent solution of alkoxysilane and/or halogenation Silang] The Si-OR machine which constitutes alkoxysilane for water required for a hydrolysis reaction, Or per [which constitutes halogenation Silang] 1mol of Si-X' groups, it adds in the quantity of 0.1-2mol preferably, and 0.1-5mol of catalysts are usually added if needed in the quantity of 0.001-1mol per alkoxysilane or 1mol of halogenation Silang. Hydrolyzate may be a partial hydrolysis thing with which the part was hydrolyzed, even if it hydrolyzes completely.

[0017] As the organic solvent in the case of using such alkoxysilane and halogenation Silang, They are mentioned by alcohols, ketone, ether, ester, and hydrocarbons and more specifically For example, alcohols, such as methanol, ethanol, propanol, and butanol, Ketone, such as methyl ethyl ketone and methyl isobutyl ketone, methyl cellosolve, Glycol ethers, such as ethylcellosolve and propylene glycol monopropyl ether, Glycols, such as ethylene glycol, propylene glycol, and hexylene glycol, Aromatic hydrocarbon, such as hydrocarbons, such as ester, such as methyl acetate, ethyl acetate, methyl lactate, and ethyl lactate, hexane, cyclohexane, and octane, toluene, xylene, and mesitylene, is mentioned.

[0018] As a catalyst, the compound in which acidity is shown in aqueous solutions, such as organic acids, such as inorganic acids, such as hydrochloric acid, nitric acid, and sulfuric acid, acetic acid, oxalic acid, and toluenesulfonic acid, or metal soap, is mentioned. As hydrolysis conditions, when hydrolyzing alkoxysilane, 80 degrees C or less of reaction temperature is 5-60 degrees C preferably, and reaction time is usually 0.5 to 5 hours preferably under churning conditions for 10 or less hours. Moreover, when hydrolyzing halogenation Silang, 50 degrees C or less of reaction temperature is 5-20 degrees C preferably, and reaction time is usually 1 to 10 hours preferably under churning conditions for 20 or less hours. Furthermore, when hydrolyzing alkoxysilane and halogenation Silang simultaneously, the hydrolysis conditions of halogenation Silang are usually adopted.

[0019] Thus, as for the obtained hydrolyzate or partial hydrolysis significant work average molecular weight (polystyrene conversion), it is desirable 500-10,000 and that it is in the range of 1,000-5,000 preferably. Its coating nature is also good while it passes through the coating liquid which will be obtained if hydrolyzate or partial hydrolysis significant work average molecular weight is in said range and it is excellent in the Tokiyasu quality.

[0020] Such a silicon compound and its hydrolyzate are SiO2 conversion, and it is desirable to be preferably contained in 10 to 25weight % of the range five to 40weight % in coating liquid.
(B) organic template material -- next as organic template material used for this invention, what is expressed with a following general formula (III) is mentioned.
[0021]
[R1R2R3R4N]+Y- (III)
Among a formula, the carbon number may differ among the hydrocarbon group of 1-20, R2, R3, and R4 mutually, or it may be the same, and H atom or a carbon number may be the hydrocarbon group of 1-20, and that of R1 may be still the same as that of R1. Y shows a halogen atom or OH group.
[0022] Such organic template material is easily removed by heat-treatment after silica system coat formation. For this reason, after organic template material is removed, the pore of a uniform size comparable as organic template material is formed into a silica system coat, and the silica system coat of low permittivity and high coat hardness can be obtained. Specifically, it is as such organic template material, Tetraethylammonium hydroxide, a tetraethylammonium star's picture, Tetraethyl ammoniumchloride, tetrapropylammonium hydroxide, A tetrapropylammonium star's picture, tetrapropylammonium chloride, n-hexadecyl trimethylammonium hydroxide, an n-hexadecyl trimethylammonium star's picture, n-octadecyl trimethylammonium hydroxide, n-octadecyl trimethylammonium star's picture, etc. can be mentioned.
[0023] If Y uses the organic template material (it becomes an organic base in this case) which is OH group, especially in order to act also as a condensation catalyst of said alkoxysilane in coating liquid and/or halogenation Silang, or such hydrolyzates When bridge formation advances and alkoxysilane and/or halogenation Silang, or such hydrolyzates have End SiH especially, conversion is effectively carried out to precise polysiloxane structure, and the silica system coat which has high coat hardness is obtained.
[0024] As for the amount of such organic template material used, it is desirable that it is in 10 to 200weight % of the range of the weight when converting the silica system component in coating liquid into SiO2. When the amount of the organic template material used is less than 10 weight %, it becomes inadequate forming of the pore of a size comparable as organic template material, and the silica system coat whose permittivity is low enough may not be obtained.
[0025] When the amount of the organic template material used exceeds 200 weight %, it is in the tendency for the hardness of the silica system coat which formation of a pore increases too much and is obtained to fall.
(C) polysiloxane -- such coating liquid for low permittivity silica system coat formation It is desirable that polysiloxane which is the reactant of one or more sorts of silicon compounds

chosen from the group which consists of halogenation Silang shown with the alkoxysilane and the following general formula (II) which are furthermore shown with a following general formula (I) and/or such hydrolyzates, and silica system particles is included.

[0026] XnSi(OR)4-n (I) XnSiX'4-n (II) (the inside of a formula, and X -- a hydrogen atom, a fluorine atom or the alkyl group of a carbon number 1-8, a fluorine substituted alkyl group, an aryl group, or a vinyl group) It expresses, R expresses a hydrogen atom or the alkyl group of a carbon number 1-8, an aryl group, or a vinyl group, and X' expresses a halogen atom. Moreover, n is the integer of 0-3.

Silica system particles can mix more than a kind of the alkoxysilane of said general formula (I) to an organic solvent, and can obtain it a hydrolysis and by carrying out condensation polymerization under existence of water and ammonia. As alkoxysilane expressed with a general formula (I), what was illustrated in the aforementioned (A) silicon compound and its hydrolyzate, and the same thing are mentioned.

[0027] When the method of preparation of silica system particles is explained still in detail, agitating a water-alcoholic mixed solvent, alkoxysilane and aqueous ammonia are added to this mixed solvent, and there is a method of making the hydrolysis reaction of an alkoxy run cause etc., for example. Under the present circumstances, 0.5-50mol per 1mol of Si-OR groups which constitutes alkoxysilane of water is used in quantity which becomes 1-25mol preferably.

[0028] Moreover, when alkoxysilane is converted into SiO2, as for ammonia, it is desirable to blend 0.01-1mol to 1mol of alkoxysilane in quantity which becomes 0.05-0.8mol preferably. As for the hydrolysis reaction of an alkoxy run, it is desirable to carry out using heat-resistant resisting pressure containers, such as an autoclave, above 200 degrees C preferably 180 degrees C or more. Furthermore, it can also ripe at constant temperature or a higher temperature after this. The polycondensation of alkoxysilane is promoted more and the one where above-mentioned reaction temperature and/or an above-mentioned maturing temperature are higher becomes precise [the inside of a silica system particle]. If reaction and/or aging are performed at such a temperature, silica system particles become much more precise, and the remains functional group on the surface of a grain will also decrease at the same time the hygroscopic property of the grain itself falls.

[0029] Moreover, the solvent of high-boiling points, such as ethylene glycol, is added, for example to the water-alcoholic mixed solvent under churning, alkoxysilane is hydrolyzed, you may generate silica system particles and they may be grown up. If the solvent of such a high-boiling point is added at the time of a hydrolysis of alkoxysilane, the ester exchange reaction of an alkoxy group will occur, a high boiling point solvent will be incorporated into the inside of a silica particle, and porous silica system particles will be obtained.

[0030] the silica obtained by ion exchange, hydrolysis, etc. in an alkali metal silicate etc. as